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<p>We have made important progress in the last year in modeling the decay of molecular orientation in poled electro-optic materials in order to more accurately predict the evolution of the nonlinear optical response over time and are approaching a predictive description of the long time scale orientational decay of poled polymer systems. The most remarkable feature of decay measurements of the nonlinear optical response is that it appears similar over so many time scales. The breadth of the time scales involved can exceed those normally measured in dielectric relaxation measurements. Models have been developed in the dielectric literature to describe relaxation processes measured over many decades of time (or frequency). These models describe the dispersive and fractal time nature of these processes, and involve an extra parameter beyond that of a stretched exponential. Thus, one parameter defines an "average" time (frequency), and two describe the shape of the distribution of relaxation time (frequencies) above and below the "average". An example of these models includes the Havriliak-Nagami model. We have begun to analyze our current data in light of these new models, and are developing programs to take transforms between the time and frequency domain to relate dielectric measurements to nonlinear optical measurements.</p>			
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## Interim Technical Report to AFOSR

**Grant:** F49620-93-1-0202 "Thermal Relaxation Processes and Stability in Poled Electro-Optic Polymers"

**Grantee:** Kenneth D. Singer

**Grantee Institution:** Case Western Reserve University

**Date:** June 30, 1994

**Project Objective:** To better understand the orientational decay mechanisms of poled second-order NLO polymers and to develop a predictive description of the long time scale (in terms of ten of years) orientational decay of poled polymer systems.

### 1. Progress

#### 1.1. *Modeling of orientational decay*

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We have made important progress in the last year in modeling the decay of molecular orientation in poled electro-optic materials in order to more accurately predict the evolution of the nonlinear optical response over time and are approaching a predictive description of the long time scale orientational decay of poled polymer systems. The most remarkable feature of decay measurements of the nonlinear optical response is that it appears similar over so many time scales. The breadth of the time scales involved can exceed those normally measured in dielectric relaxation measurements. Models have been developed in the dielectric literature to describe relaxation processes measured over many decades of time (or frequency). These models describe the dispersive and fractal time nature of these processes, and involve an extra parameter beyond that of a stretched exponential. Thus, one parameter defines an "average" time (frequency), and two describe the shape of the distribution of relaxation times (frequencies) above and below the "average". An example of these models includes the Havriliak-Nagami model. We have begun to analyze our current data in light of these new models, and are developing programs to take transforms between the time and frequency domain to relate dielectric measurements to nonlinear optical measurements.

We have developed algorithms based on the empirical data of Stahelin et al.<sup>1</sup> which relates the ambient temperature below the glass transition temperature to expected stability. This algorithm depends on a stretched exponential. We are currently examining how to alter this algorithm to include the more appropriate model described above. The Stahelin data includes only the "average" time parameter, but not the parameter or

<sup>1</sup> M. Stahelin, D.M. Burland, M. Ebert, R.D. Miller, B.A. Smith, R.J. Twieg, W. Volksen, and C.A. Walsh, *Appl. Phys. Lett.* 61, 1625 (1992).

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parameters describing the shape of the distribution. For accurate predictions, these parameters must be included. We are currently working on this.

We have also developed a figure of merit to describe the short term stability of the electro-optic coefficient. The short term stability is determined largely by the "match" between the chromophore and the polymer...i.e. how easily does the molecule diffuse (rotationally or translationally) through the polymer. The short-term stability determines the useful nonlinearity or operating voltage of an electro-optic device over its useful life. Because larger nonlinearities are needed, it is important to eliminate this short-term decay. The figure of merit defined is the difference between the activation energy of the pure polymer and that of the chromophore contained in the polymer. For example, in some of our preliminary studies, we found that the activation energy of DRI dissolved in PMMA is half that of PMMA while a similar molecule reacted in to PMMA gives the same activation energy as pure PMMA. In the first case, a great deal of short term decay is observed while in the latter very little is observed. When the activation energies of the chromophore containing polymer is equal to the pure polymer, further stability is gained only by changing the polymer system.

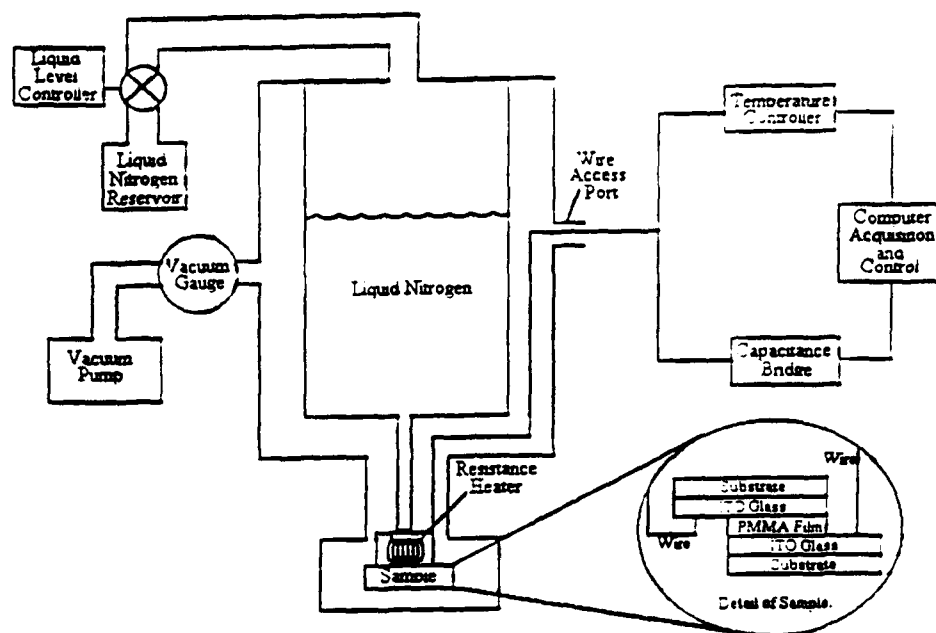
Publication of the above results awaits the accumulation, analysis, and comparison to data which is in the process of being collected, as described below.

## **1.2. Experiments**

In the past year, we have been assembling and constructing the apparatus to study in-situ poling and decay of the second harmonic coefficient as a function of temperature. We have assembled the temperature control system shown in Figure 1 which can access temperature from liquid nitrogen temperature to about 150 C. We have a separate cell which can access temperatures to 300 C. The apparatus in Figure 1 consists of a liquid nitrogen dewar with a resistance heater which is temperature controlled. This system has been built to be capable of carrying out electrical measurements concurrent with the nonlinear optical measurements. Thus, we have the capability to measure the dielectric constant, resistivity, thermally stimulated depolarization, and isothermal depolarization. These measurements will be able to characterize the relaxation behavior of the polymer over an extremely wide range of times so as to best determine the appropriate model (see above) which describes the relaxation.

In order to carry out in-situ measurements, a transparent electrode system must be arranged which is able to withstand the high power laser pulses. Sputtering of ITO on the polymer was attempted, but the thermal mismatch with the polymer led to cracking. We are currently producing samples by fusing two films deposited on ITO coated glass under temperature and pressure. These samples are currently under measurement. These measurements include the electrical and second harmonic measurements as well as measurements of the electro-optic effect.

Our initial measurements involve DR1 in PMMA, but will later include a reacted in system from IBM, a polyimide system from Amoco, and eventually, the cross-linked system from USC. We are currently collecting data on the DR1 in PMMA system.



**Figure 1.** Experimental dewar system

### 1.3. Laser System

We have built a new tunable laser source for harmonic generation experiments. The system uses a synchronously pumped OPO which is pumped by a train of 10 psec mode-locked pulses generated in an active-passive negative-feedback mode-locked Q-switched configuration. We have observed significant pulse compression when the OPO is slightly detuned from synchronicity. This pulse compression can not only result in sub-picosecond pulses, but also very high intensity pulses appropriate for nonlinear optical measurements. This compression arises from the group velocity mismatch of the pump and generated pulses in the nonlinear crystal. The compression takes place at a pump level well above threshold which is very important for the stability of the OPO operation.

Our synchronously pumped OPO was built using two BBO crystals (10 mm each) and pump - steering mirrors. The pump radiation is the third harmonic of a pulsed Nd:YAG laser with hybrid active-passive mode-locking and passive negative feedback. Pump radiation consists of about 40 pulses with the duration of about 11 picoseconds. The threshold pump pulse energy varies with the generated wavelength and was found to be 4

- 10  $\mu$ J. Figures 2 and 3 shows experimental and theoretical results, obtained at an oscillating wavelength of 1300 nm and at a pump level exceeding the oscillation threshold by 6 times. The conversion efficiency at this pump level is about 10% which corresponds to internal efficiency of 40%. At zero cavity detuning (which corresponds to the minimum threshold intensity) the generated pulses had their maximum duration of about 11 ps. When the cavity was longer by approximately 0.3 mm, the pulse duration was only about 2.5 - 3 ps with nearly no loss of pulse energy.

According to our model, the compression occurs due to the favorable amplification of the leading edge of the generated pulse which is moving faster than the pump pulse in the crystal (because of the crystal birefringence). The compression is optimized when the group velocity walk-off in the crystal is of the order of the pump pulse duration and the cavity mismatch is about 10% of the walk-off. The OPO's generation bandwidth is defined mostly by the interaction length in the crystals and in our case can lead to compression producing pulses as short as about 500 fs far away from the degeneracy point.

We have used this laser system to study the contribution of the lowest lying Ag state to the third order optical nonlinearity in squaraine dyes in collaboration with workers at NASA Lewis Research Labs (under partial NASA funding). We have found that the lowest-lying two-photon state make a significant contribution to the optical nonlinearity in contradiction to quantum chemical calculations. These results have a significant impact on the potential applicability of such dyes in third order devices in the visible and near-infrared as this two-photon state leads to significant two-photon absorption. Our results show that the spectral range for potential applications is limited.

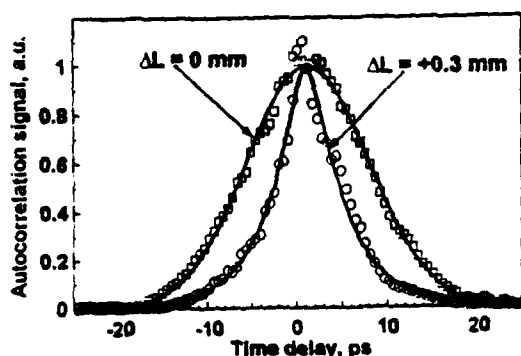


Figure 2. Autocorrelation functions of the oscillating pulse at zero cavity length detuning  $\Delta L = 0$  (squares - experiment, solid line - best fit using symmetric Gaussian pulse shape, FWHM pulse duration  $\Delta\tau = 10.7$  ps) and at  $\Delta L = +0.3$  mm (circles - experiment, solid line - best fit using asymmetric double-exponential pulse shape,  $\Delta\tau = 2.9$  ps).

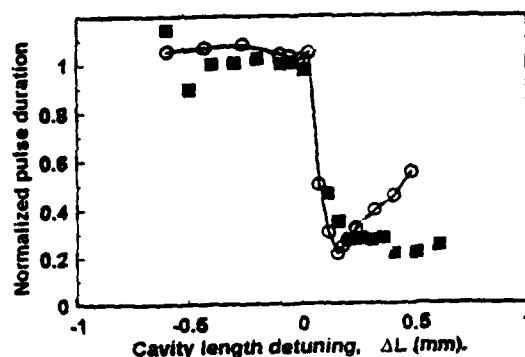


Figure 3. Dependence of the oscillating pulse duration on  $\Delta L$ . The duration is normalized to the pump pulse FWHM duration. (Open circles - numerical simulations, filled squares - experiment)

## **2. Publications and Lectures on AFOSR Funding**

### **2.1. Invited Lectures**

1. K.D. Singer, "Orientational Relaxation Phenomena in Electro-optic Polymers", Gordon Research Conference on Dielectric Phenomena, Holderness School, NH July 31-August 5, 1994.
2. K.D. Singer, R. Dureiko, J. Khaydarov, and R. Fuerst, "Relaxation in Poled Electro-optic Polymers", 4th Iketani Conference, Hawaii, May 17-20, 1994.
3. J.H. Andrews, J.D.V. Khaydarov, and K.D. Singer, "Third Harmonic Dispersion Studies of a Squarate Dye: Probing the  $2^1\text{Ag}$  State", ICONO'1, Val Thorens, France, January, 1994.
4. K.D. Singer, R. Dureiko, J. Khaydarov, and R. Fuerst, "Relaxation Phenomena in Poled Electro-Optic Polymers", *Proc. Mat. Res. Soc.* **328**, 499 (1994).
5. R.A. Fuerst, "Thermal Relaxation Processes and Stability in Poled Electro-optic Materials", Research Project Symposium Day, Ohio Space Grant Consortium, Ohio Aerospace Institute, Cleveland, OH.

### **2.2. Submitted Lectures**

1. J.D.V. Khaydarov, J.H. Andrews, and K.D. Singer, "Dispersive Pulse Compression in a Synchronously Pumped Optical Parametric Oscillator", CLEO, Anaheim, CA. May 8-13, 1994.
2. J.H. Andrews, J.D.V. Khaydarov, and K.D. Singer, "Third-harmonic Dispersion Studies of a Squarate Dye: Probing the  $2^1\text{Ag}$  State", IQEC, Anaheim, CA. May 8-13, 1994.

### **2.3. Journal Publications**

1. J.H. Andrews, J.D.V. Khaydarov, K.D. Singer, D.L. Hull, and K.C. Chuang, "Spectral Dispersion of Third Harmonic Generation in Squaraines", *Nonlinear Optics*, in press.
2. J.H. Andrews, J.D.V. Khaydarov, and K.D. Singer, "Contribution of the  $2^1\text{Ag}$  State to the Third Order Optical Nonlinearity in a Squaraine Dye", *Opt. Lett.*, in press.

3. J.D.V.Khaydarov, J.H. Andrews, and K.D. Singer, "Pulse Compression in a Synchronously Pumped Optical Parametric Oscillator Due To Group Velocity Mismatch", *Opt. Lett.* **19**, 831 (1994).
4. K.D. Singer and J.H. Andrews, "Origin of Third-order Optical Nonlinearities in Centrosymmetric Organic Materials", *Condensed Matter News* in press.
5. J.D.V. Khaydarov, J.H. Andrews, and K.D. Singer, "20-Fold Pulse Compression in a Synchronously Pumped Optical Parametric Oscillator", *Appl. Phys. Lett.* submitted.